Disordered Rocksalt Transition-Metal Oxides (TMOs): Synthetic Strategies

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2019 DOE VTO Annual Merit Review
June 11, 2019

Project ID: bat406

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Overview

Timeline

- Start date: October 2018
- End date: September 2021
- Percent complete: 10%

Budget

- Total project funding
  - FY19 $3.7 M
- BAT376, BAT404, BAT405 and BAT406 (LBNL, ORNL, PNNL, UCSB)

Barriers Addressed

- Energy density
- Cycle life
- Cost

Partners

- Lawrence Berkeley National Laboratory
- Oak Ridge National laboratory
- Pacific Northwest National Laboratory
- UC Santa Barbara

Relevance/Objectives

- Cathode materials based on cation-disordered Li-excess rocksalts (DRX) can deliver energy densities up to 1000 Wh/Kg.
- DRX structure allows a wide range of chemistry, providing an opportunity to develop Co-free high energy density cathode materials that are alternative to the traditional layered NMC-type cathodes.
- Fundamental understandings on what controls DRX performance characteristics, particularly rate capability, cycling stability and voltage slope, are key to enabling rational decisions on further development and commercial viability of this newer class of cathode materials.

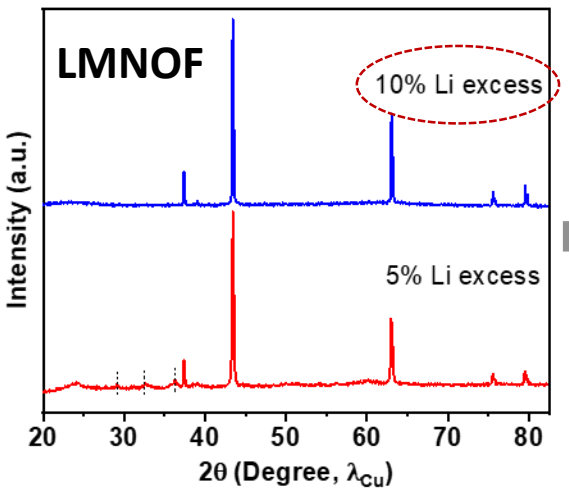
Milestones

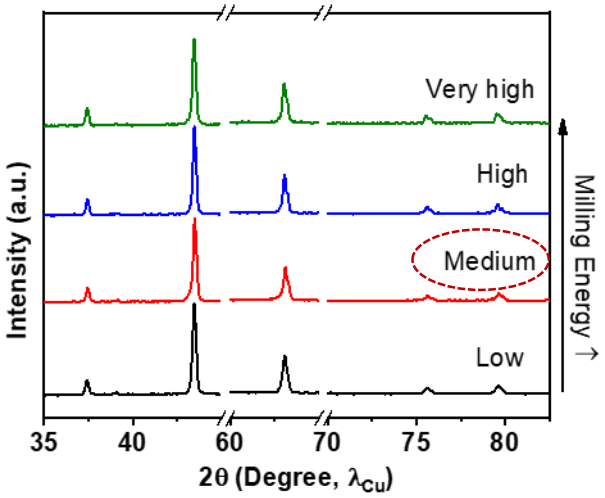
Date	Milestones	Status
December 2018	Held all-hands team meeting and agreed synthesis and testing protocols.	Completed
March 2019	Synthesis (10 g minimal) of at least 2 DRX compositions.	Completed
June 2019	Go/No-Go: Novel method for high fluorination. No-Go if F-content cannot be > 7.5%; then revert to solid-state synthesis.	On schedule
September 2019	Pouch cell evaluation of DRX materials. Report key performance metrics on one of the rocksalt materials.	On schedule

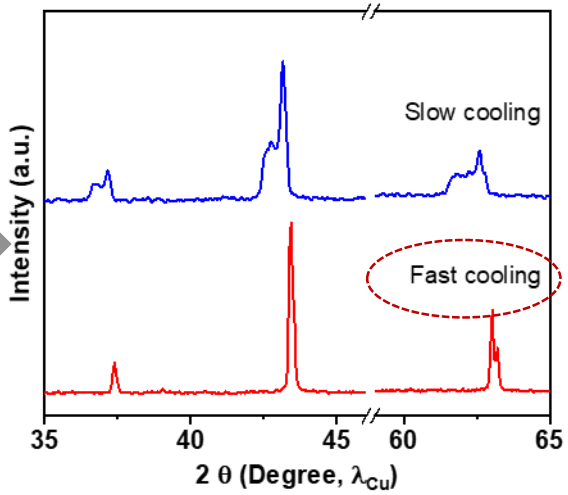
Approach/Strategy

- Focus on three DRX baseline systems and their analogues: $Li_{1.2}Mn_{0.625}Nb_{0.175}O_{1.95}F_{0.05}$ (LMNOF), $Li_{1.15}Ni_{0.45}Ti_{0.3}Mo_{0.1}O_{1.85}F_{0.15}$(LNTMOF) and $Li_2Mn_{1/2}Ti_{1/2}O_2F$ (LMTOF).
- Explore synthesis conditions to prepare DRX materials with optimized performance. Establish reliable and scalable synthesis protocols and provide same-batch materials to the tasks within the DRX program.
- Fabricate quality electrodes of DRX materials. Develop electrochemical testing protocols and benchmark DRX performance metrics.
- Develop, synthesize and characterize DRX model systems for mechanistic understanding and experimental support of the modeling effort.

Technical Accomplishments: solid-state synthesis optimized

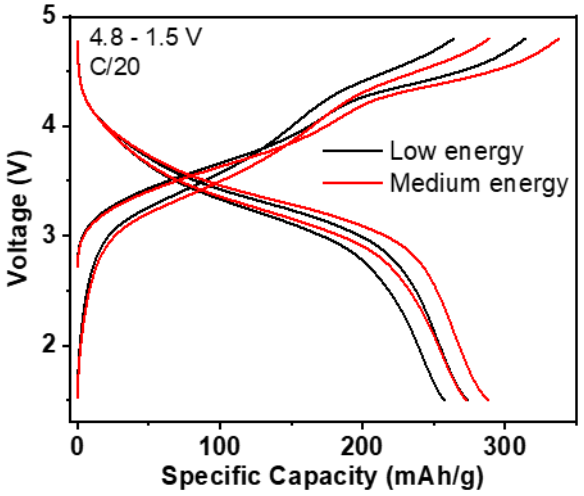


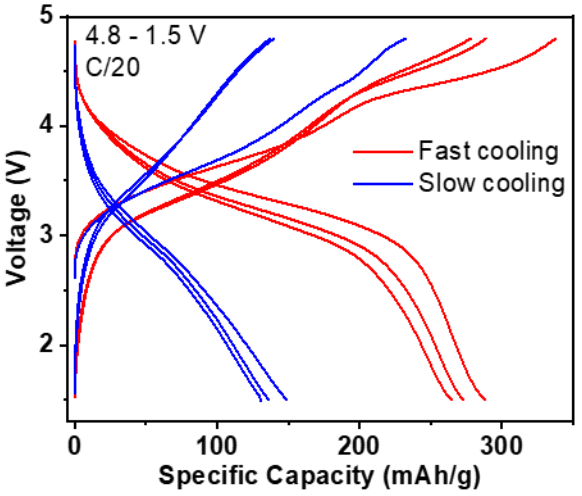




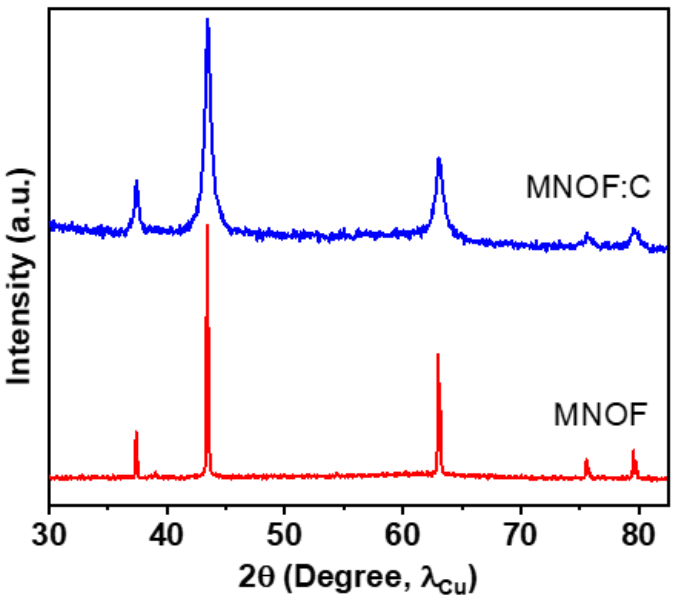
Optimal conditions highlighted in red circles

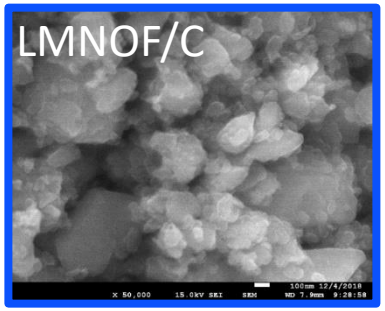
- Solid-state synthesis conditions for LMNOF were optimized on precursors and calcination conditions.
- Cooling rate shows much larger impact on phase formation and electrochemistry than precursor mixing.

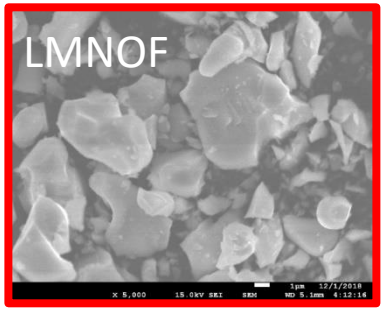




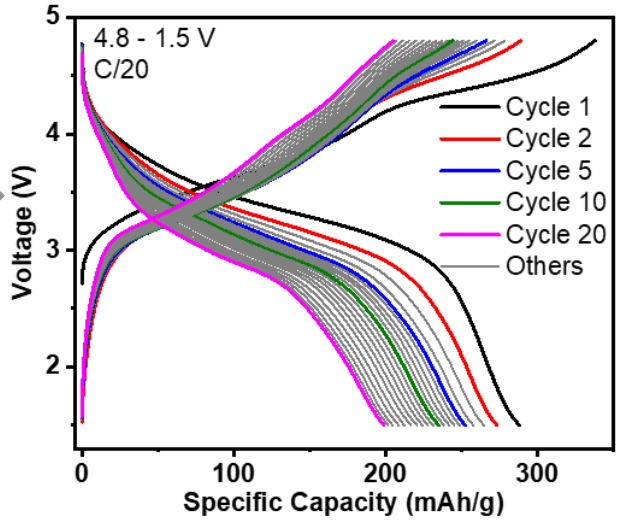
Optimized LMNOF synthesized at 10 g scale

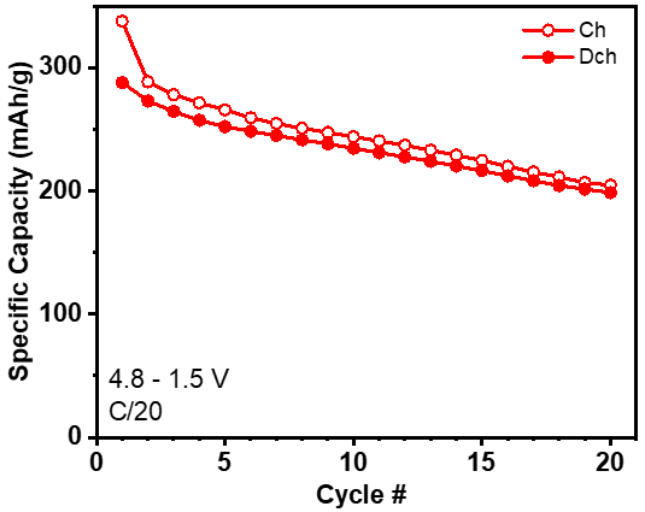






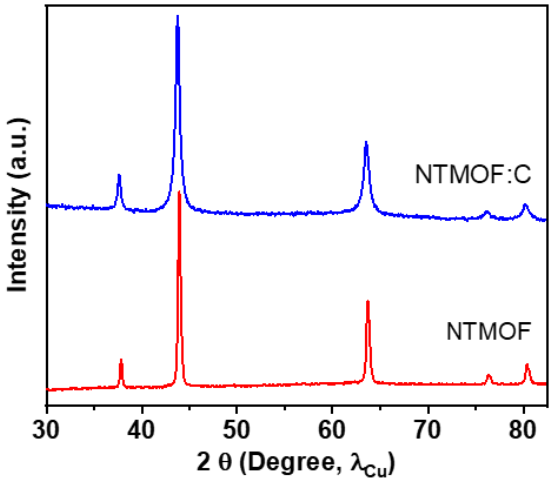
$Li_{1.2}Mn_{0.625}Nb_{0.175}O_{1.95}F_{0.05}$ (MNOF)	Theo. Cap. (mAh/g)
Mn^{3+}/Mn^{4+}	184
1 Li^{+}	294
1.2 Li^{+}	353

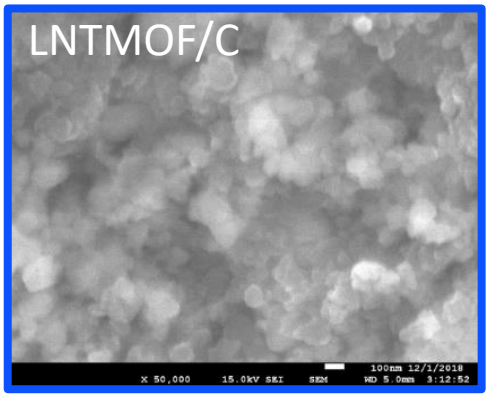


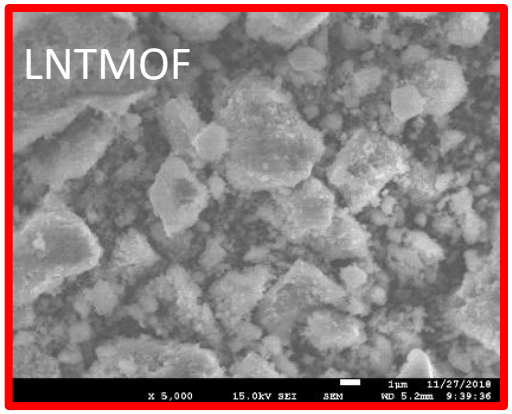


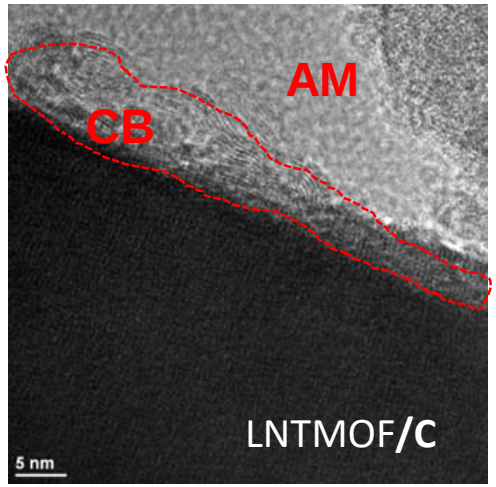
- Phase-pure LMNOF synthesized at 10 g scale, providing 1st baseline material for the DRX program.
- LMNOF/C composite with a size of a few hundred nm delivered an initial capacity of 288 mAh/g.

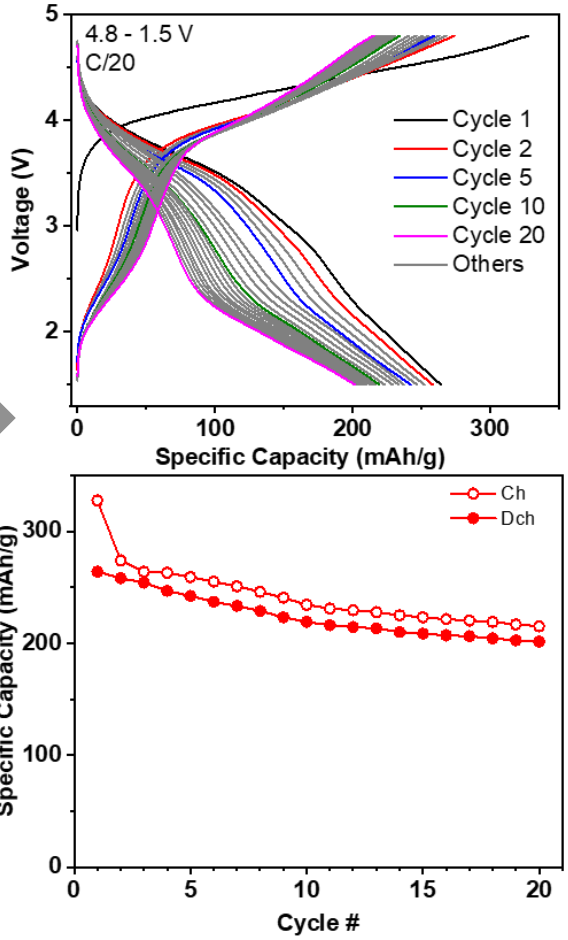
Optimized LNTMOF synthesized at 10 g scale









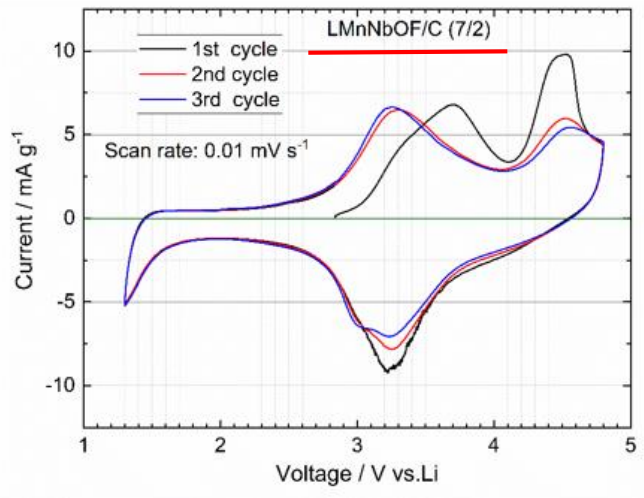


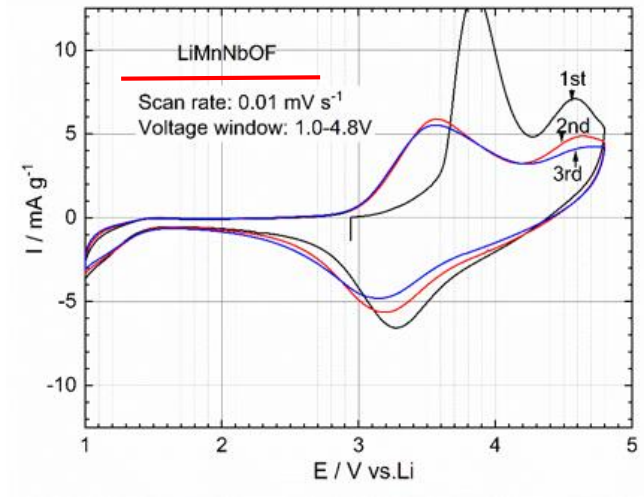
- Phase-pure LNTMOF produced at 10 g scale, providing 2nd baseline material for the DRX program.
- LNTMOF/C composite with a particle size of ~300 nm prepared. TEM reveals a thin carbon layer as a result of ball-milling.

$Li_{1.15}Ni_{0.45}Ti_{0.3}Mo_{0.1}O_{1.85}F_{0.15}$ (LNTMOF)	Theo. Cap. (mAh/g)
Ni^{2+}/Ni^{4+}	266
1 Li^{+}	295
1.15 Li^{+}	340

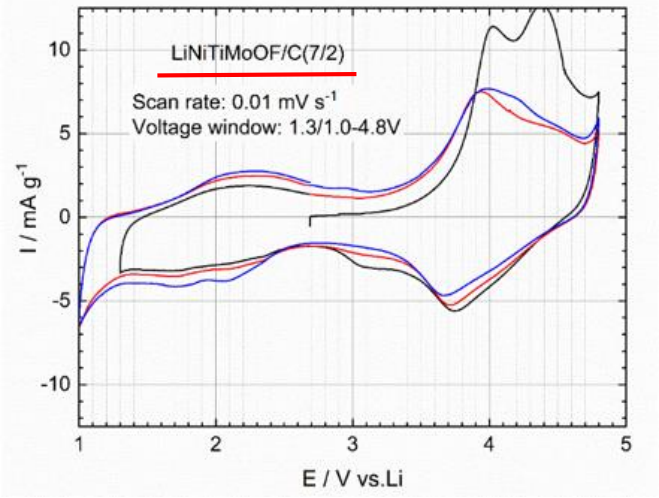
Electrochemical behavior evaluated

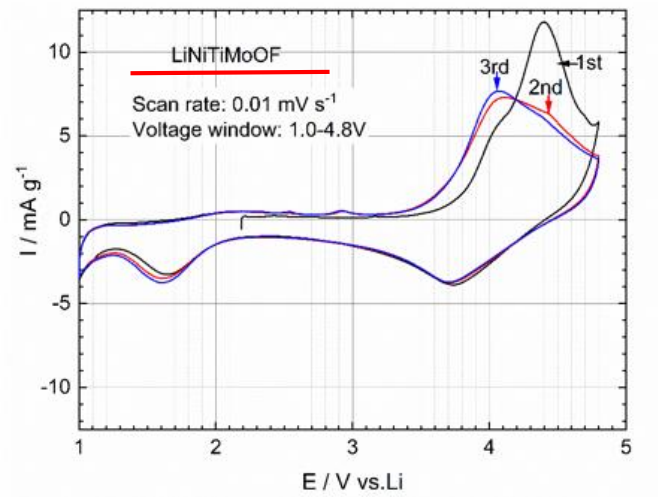
LMNOF
w/ and w/o CB ball milling





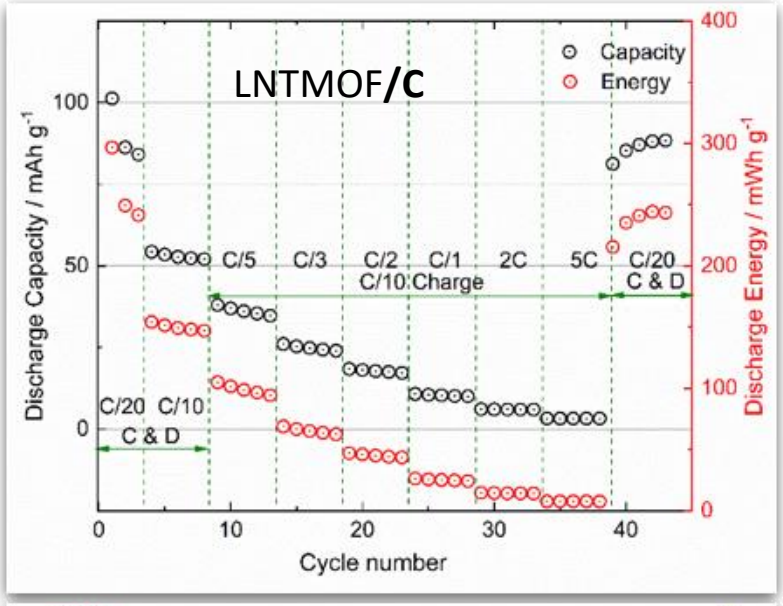
LNTMOF
w/ and w/o CB ball milling

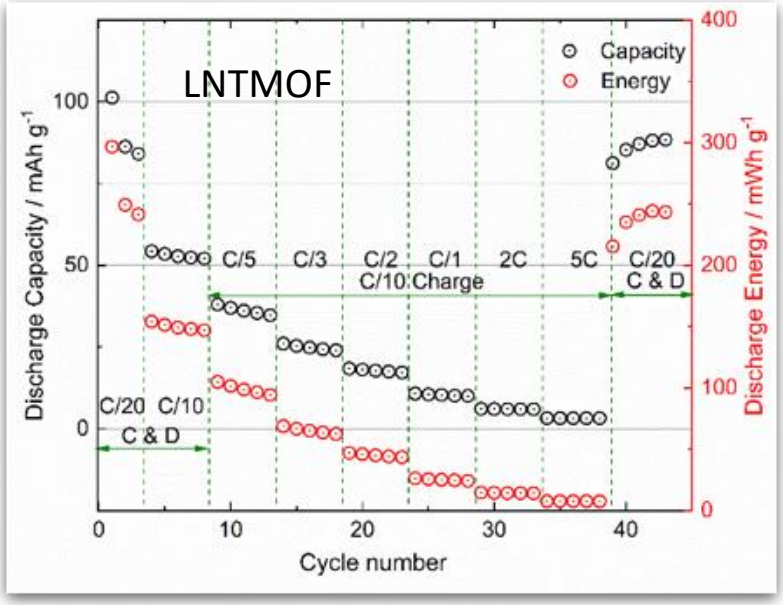


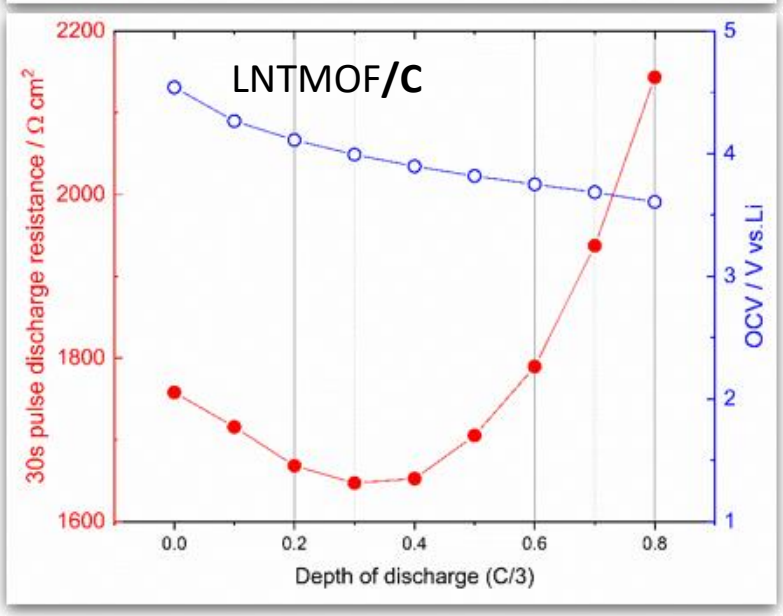


- Electrochemistry evaluated in half-cells with a Gen 2 electrolyte.
- Significant difference in electrochemical response during the first anodic scan and the following anodic scans, suggesting irreversible changes.
- LNTMOF shows more voltage hysteresis than LMNOF, but overall less voltage hysteresis in materials with ball-milled carbon-black.

Rate performance evaluated

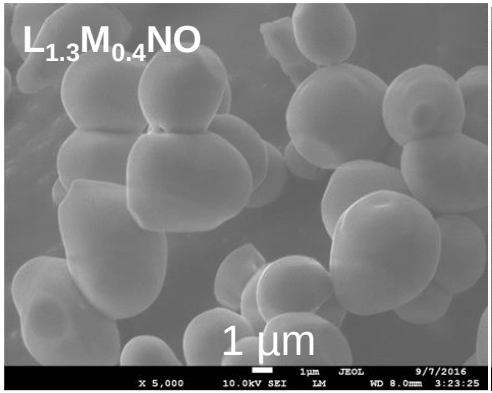


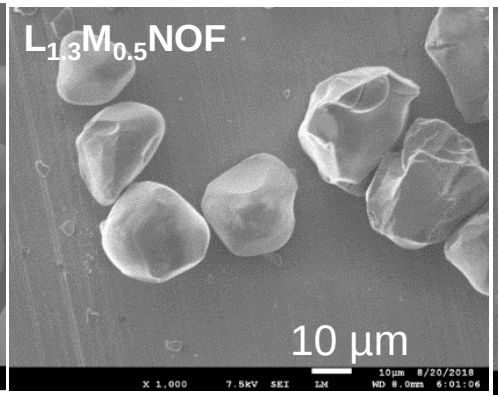


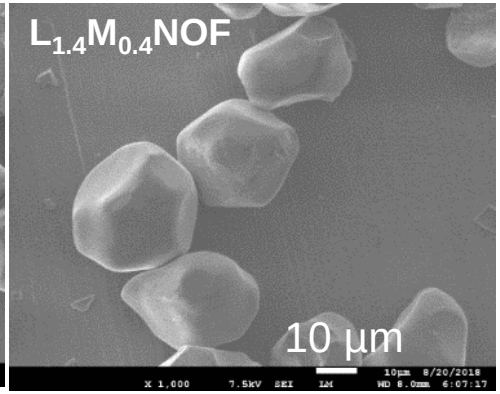


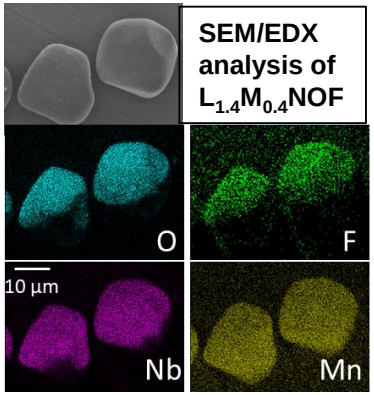
- LNTMOF and LNTMOF/C assessed for complete discharge performance and 30s pulse-power performance *vs*. DOD.
- Both samples with and without carbon show capacity decrease with increasing rate, signaling high resistance.
- OCVs were above 3.6 V down to at least 80% DOD of LNTMOF, suggesting most capacity is at a fairly high voltage but poor Li transport leads to large over-potential.

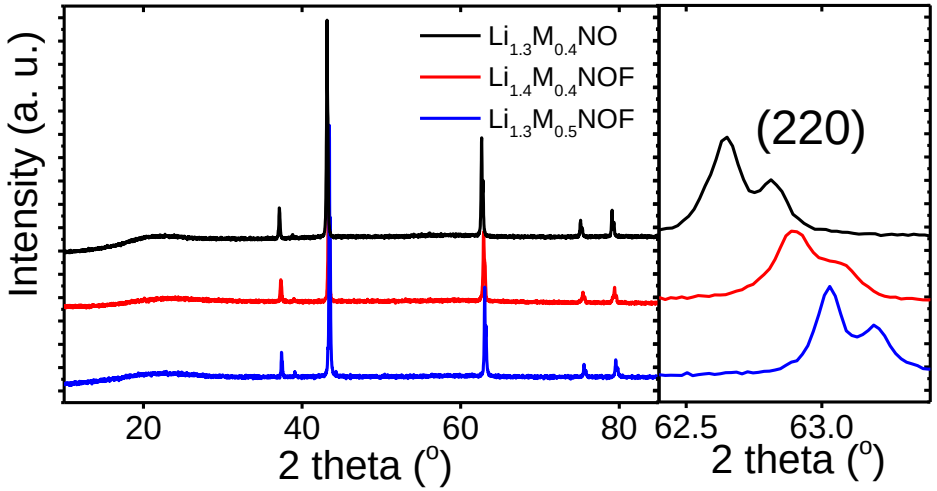
Optimization of F content in DRX







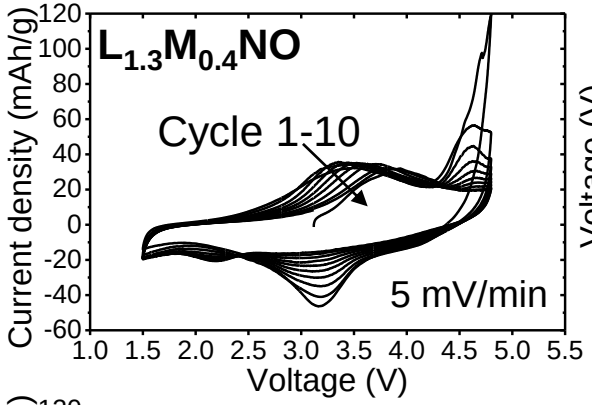


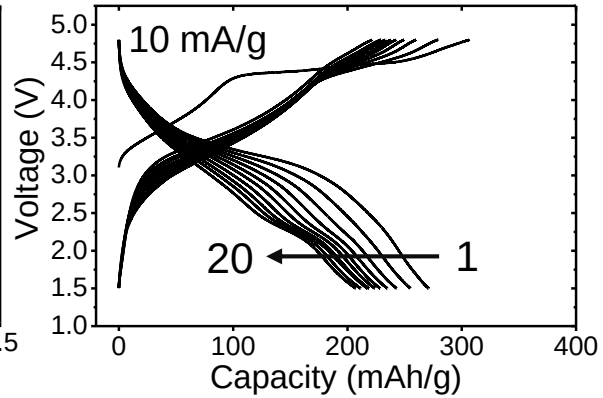


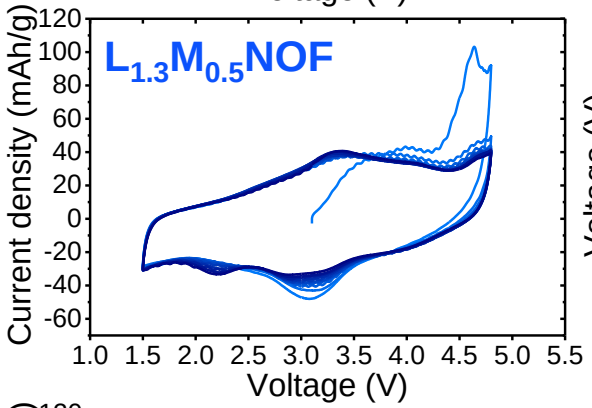
Compound	Theo. Cap. $Mn^{3+/}Mn^{4+}$ (mAh/g)	Theo. Cap. Li content (mAh/g)
$Li_{1.3}M_{0.4}NO$	118.00	383.49
$L_{1.3}M_{0.5}NOF$	152.87	397.46
$L_{1.4}M_{0.4}NOF$	128.44	449.57

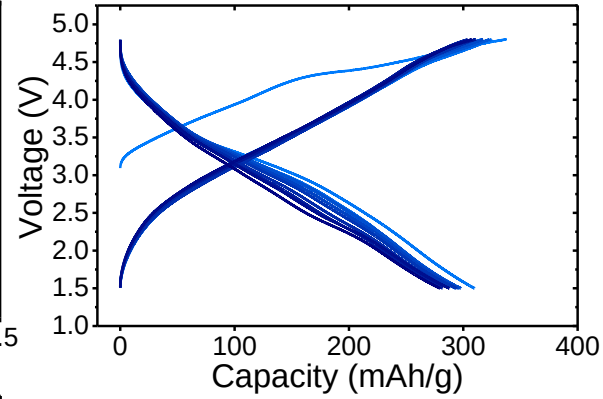
- Molten-salt method was used to synthesize phase-pure, discrete crystal samples of LMNOF analogues with various F substitution levels: $Li_{1.3}Mn_{0.4}Nb_{0.3}O_2$ ($L_{1.3}M_{0.4}NO$), $Li_{1.3}Mn_{0.5}Nb_{0.2}O_{1.8}F_{0.2}$ ($L_{1.3}M_{0.5}NOF$) and $Li_{1.4}Mn_{0.4}Nb_{0.2}O_{1.6}F_{0.4}$ ($L_{1.4}M_{0.4}NOF$). Note F content to be verified.
- Synthesized DRX model samples used to investigate the role of F in DRX performance and stability.

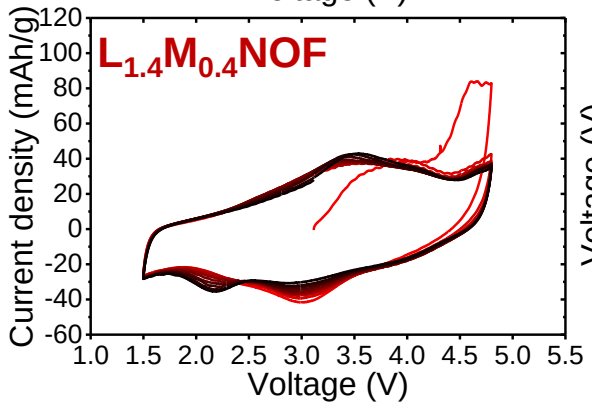
F enhances electrochemical performance

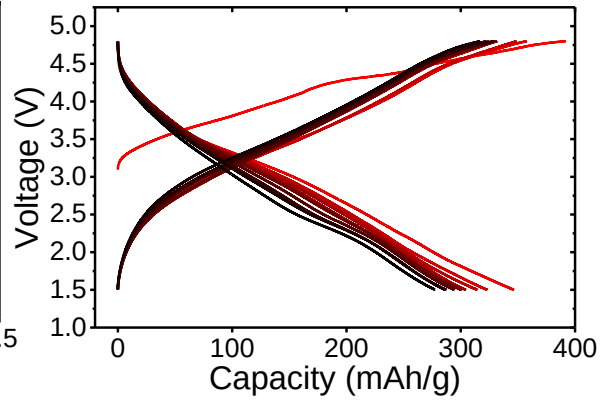


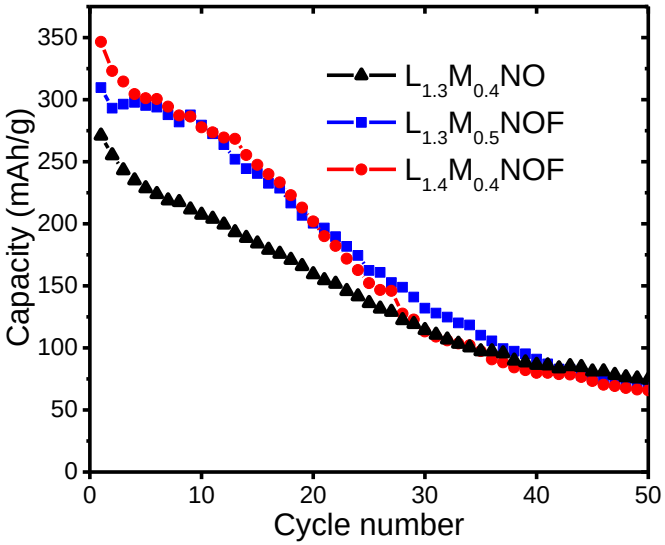








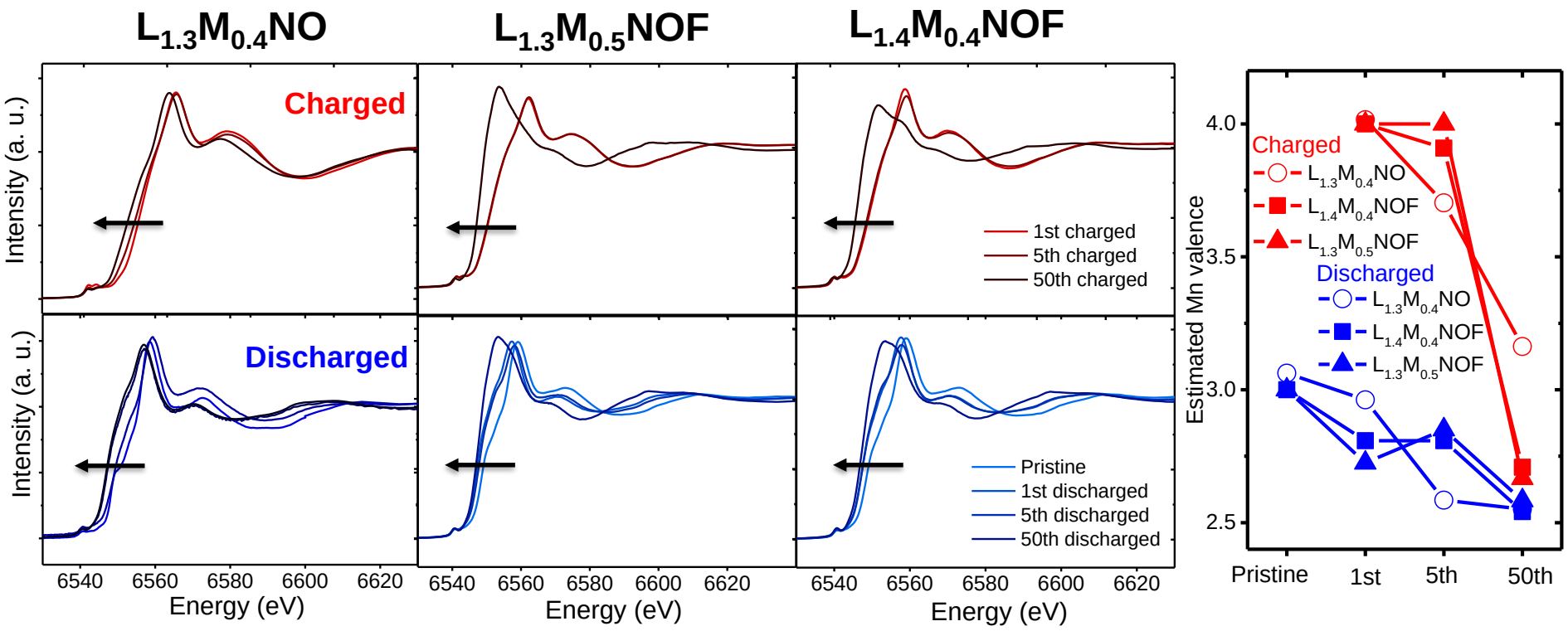




- Oxide capacity decreases continuously with cycling.
- In fluorinated samples, capacity retention much improved during initial cycling. But the improvement did not last upon extensive cycling.

F improves chemical stability of redox-active Mn

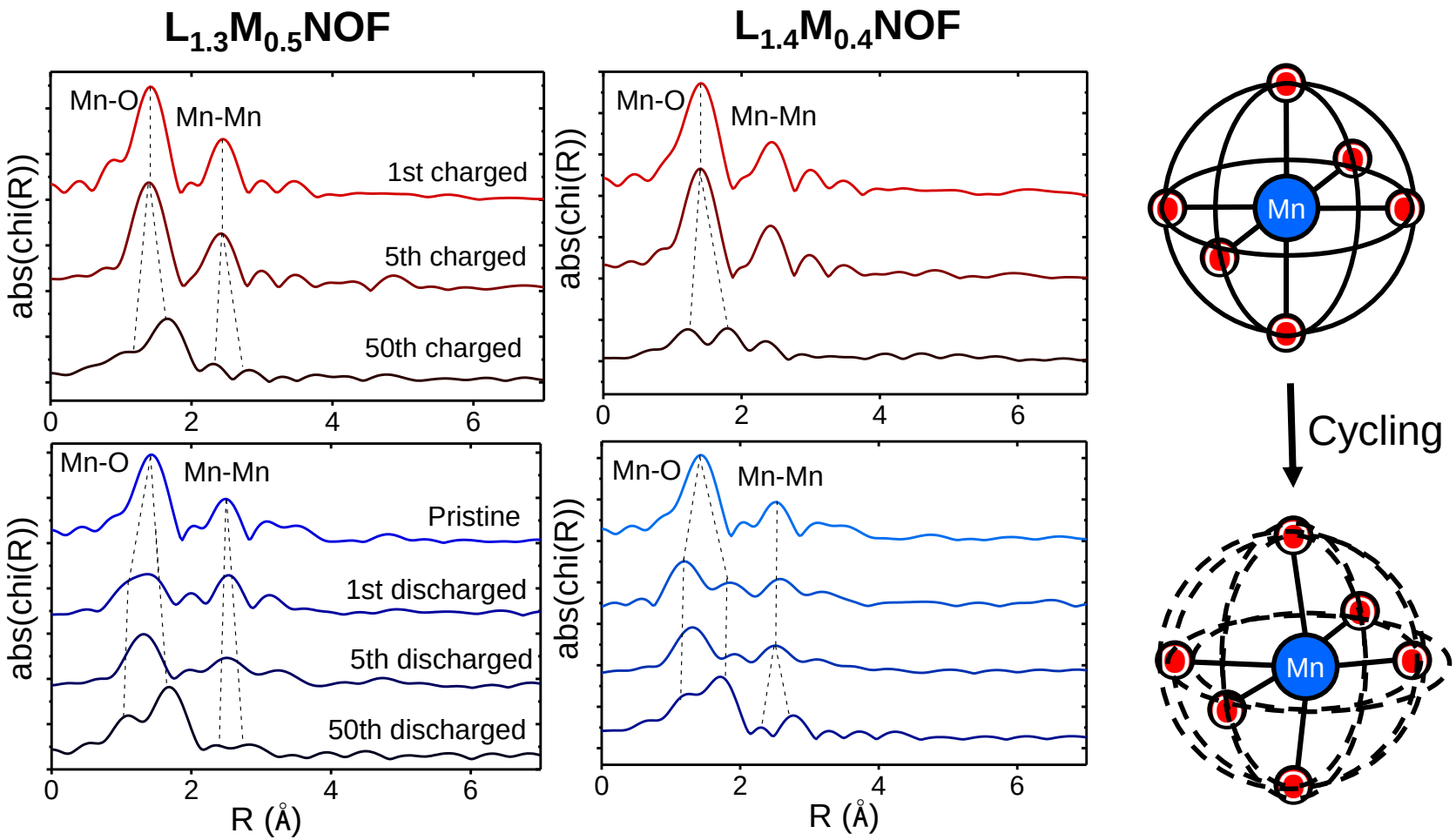
Mn K-edge hard XAS/XANES spectra *(SSRL beamline 2-2)*



- Bulk Mn reduced upon cycling of the oxide. Lower Mn oxidation state at both charged and discharged states with each cycle.
- In fluorinated samples, bulk Mn reduction less severe during initial cycling.

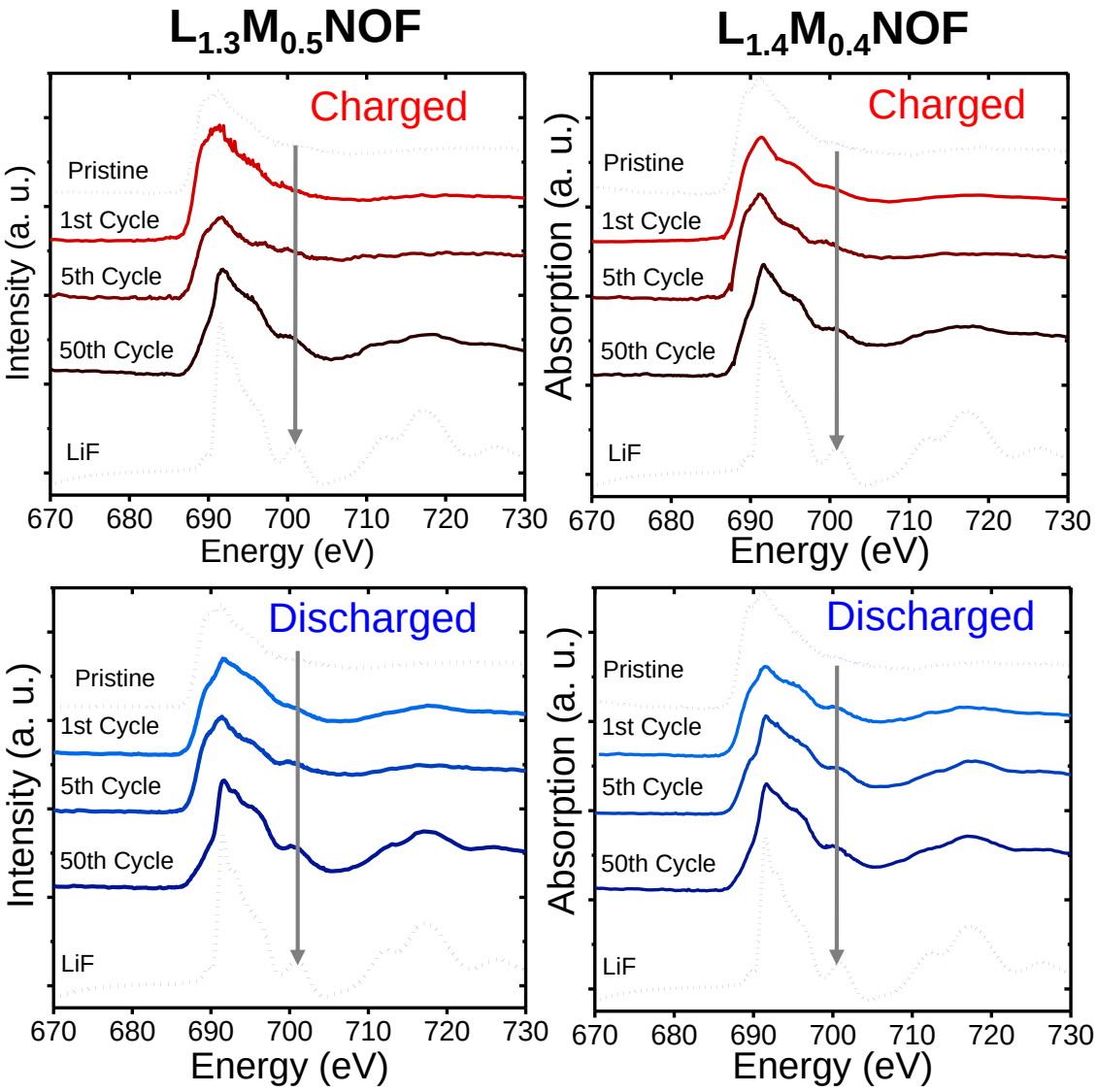
F improves structural stability of redox-active Mn

Mn K-edge hard XAS/EXAFS spectra *(SSRL beamline 2-2)*

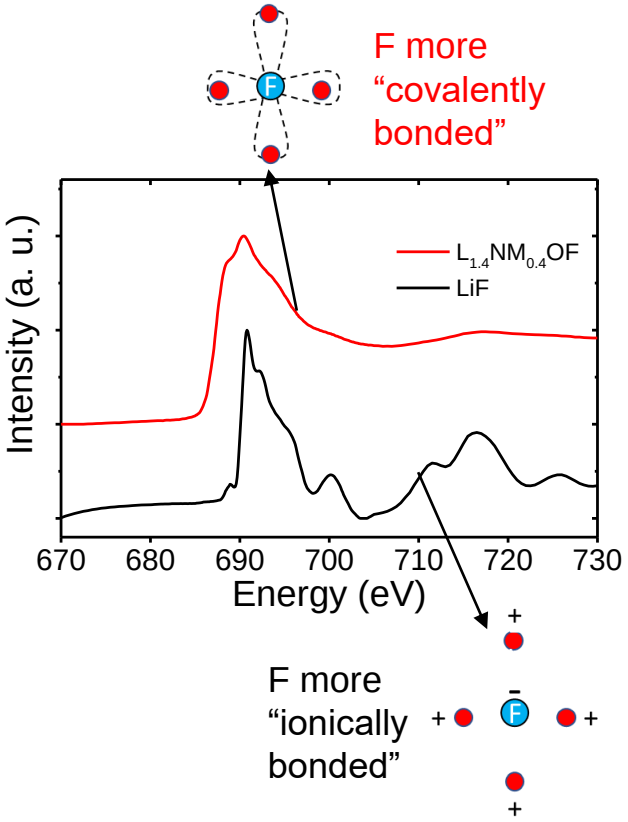


- Intensities of Mn-O and Mn-Mn peaks in both charged and discharged samples decrease with cycling, suggesting a reduction in structural coordination.
- In fluorinated samples, these changes occurred at a much slower rate.

Chemical nature of surface F evolves with cycling

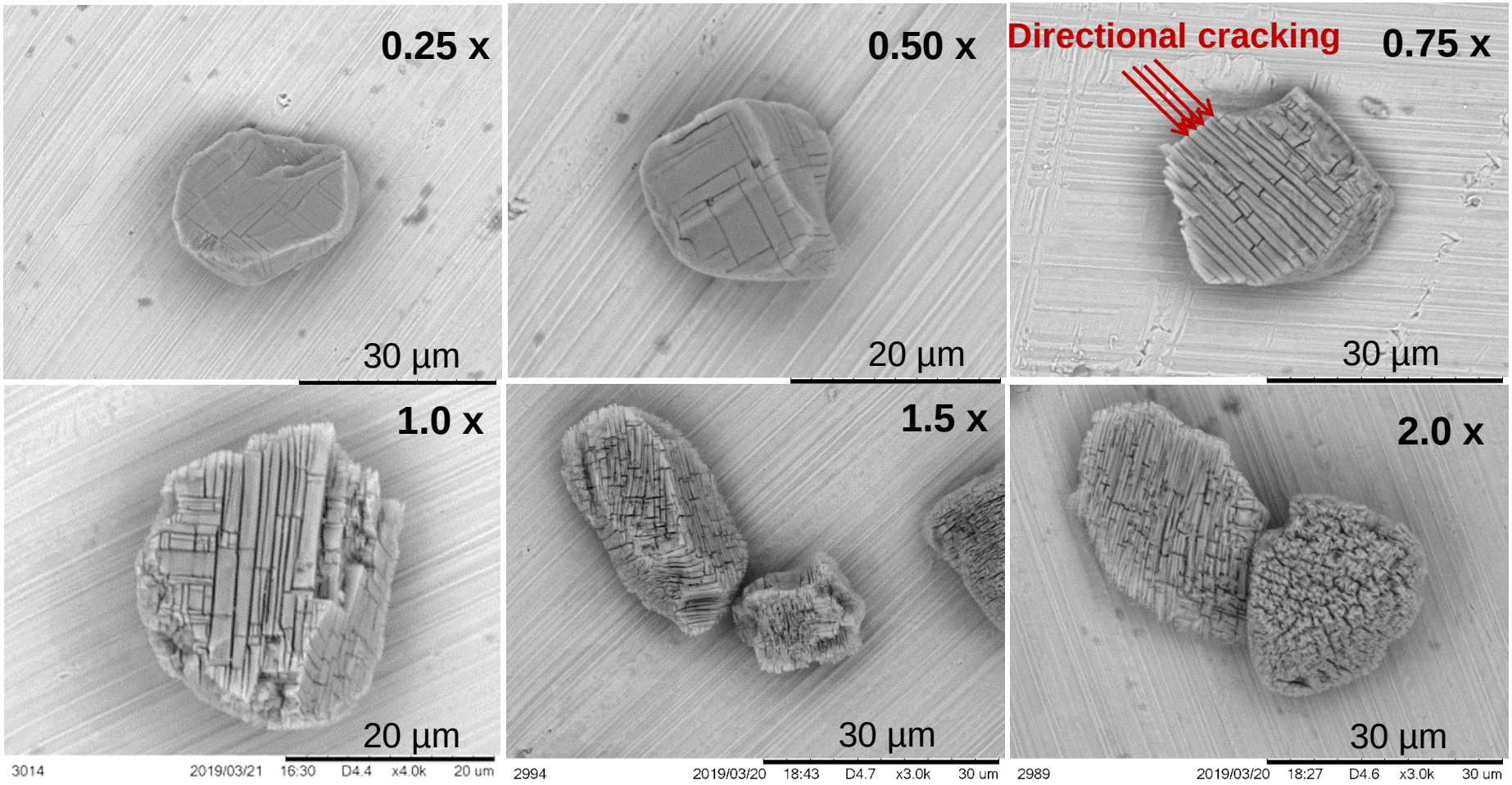


TEY F K-edge XAS *(SSRL BL 8-2)*



- With cycling, surface F (top 5 nm or so) becomes more "LiF-like". Mechanism to be investigated.

Morphology damage upon DRX delithiation



- 0.25 x, 0.5 x, 0.75 x, 1.0 x, 1.5 x and 2.0 x samples were prepared by chemical reactions between NO_2BF_4 and $L_{1.4}M_{0.4}NOF$ at the indicated mole ratio. A higher ratio corresponds to more Li extraction.
- Single-particle level cracking observed upon Li removal. Extent of cracking increases with delithiation.
- Cracking appears to be directional. Mechanistic implication to be investigated.

Responses to Previous Year Reviewers' Comments

This is a new project.

Contributors and Acknowledgement

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Remaining Challenges and Barriers

- Knowledge of what controls DRX cycling stability and how can it be improved.
- Knowledge of what controls DRX rate capability and how can it be improved.
- Knowledge of what controls DRX voltage slope and to what extent it can be reduced.
- Understand other performance issues that may pose challenges to commercial adoption of DRX cathode materials.

Proposed Future Work

- Explore processing conditions of adding carbon to DRX, both during synthesis and electrode fabrication. The goal is to minimize resistance in DRX.
- Develop reliable synthesis protocols to scale up DRX batch size to 50 g which is needed for a more rounded effort in materials evaluation.
- Investigate DRX rate capability and determine key barriers in kinetics
  - Pouch cell evaluation on power density of at least 2 DRX compositions.
  - Determine the source of impedance at different depths of discharge.
  - Determine the onset of poor transport properties.
- Understand the role of F in rate capability, stability and voltage profiles of DRX cathodes for F content optimization.

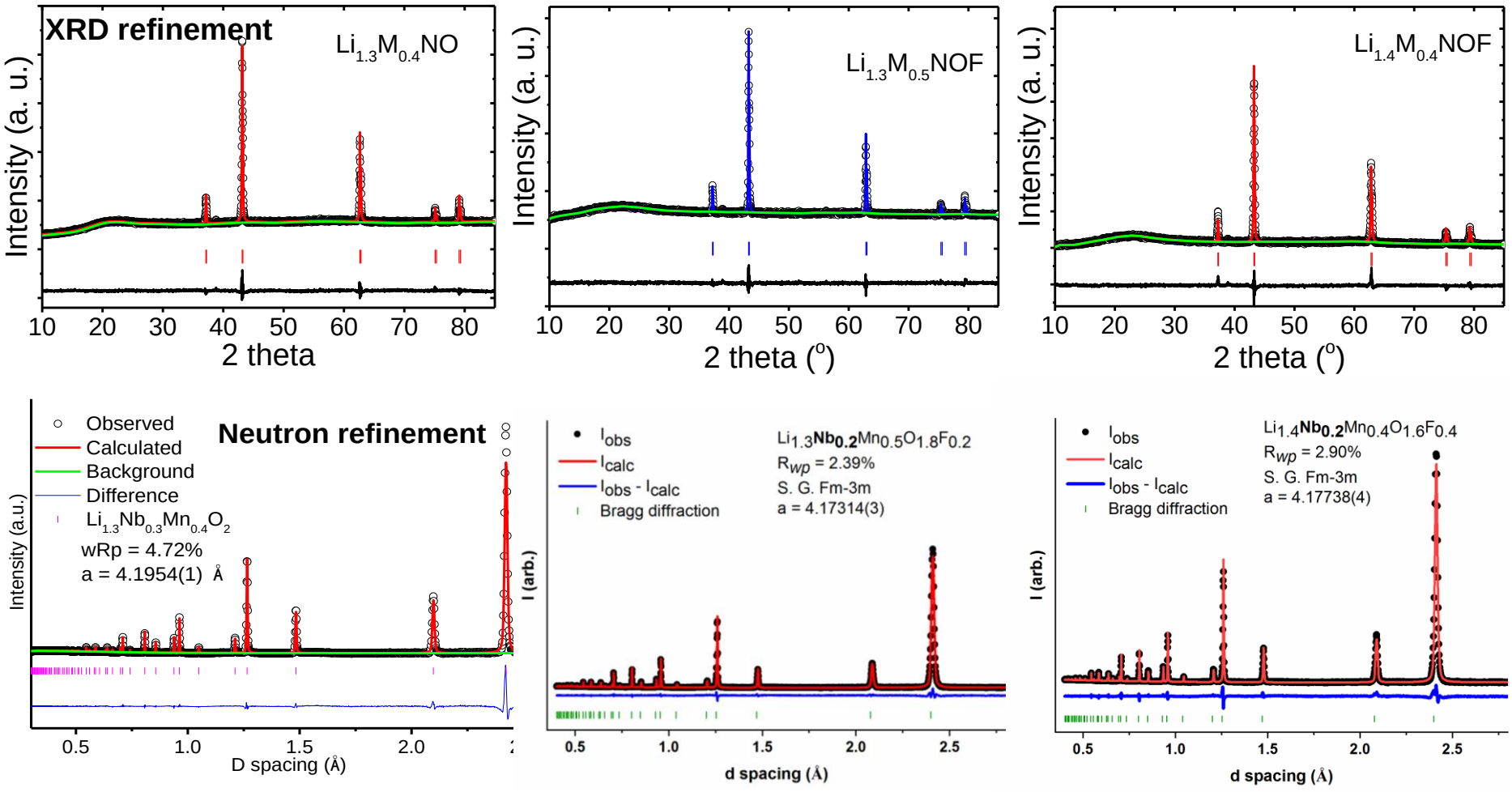
"Any proposed future work is subject to changes based on funding levels."

Summary

- Solid-state reaction conditions for DRX synthesis optimized.
- Two DRX samples were prepared at 10 g scale, suitable for use as baseline materials for the tasks within the program.
- DRX electrode fabrication process investigated and electrochemical performance evaluated.
- Model samples with varying F content synthesized in discrete crystals. F was found to improve electrochemical performance, chemical and structural stabilities of DRX during initial cycling.
- Single-particle based studies revealed morphology damage with Li extraction from DRX.

Technical Back-Up Slides

Rietveld refinements



- XRD and neutron refinements confirm that synthesized DRX crystal samples were phase-pure rocksalts with a cation-disordered structure.

Electrode fabrication and cell testing conditions

- Electrodes fabricated with active material/carbon black/PVDF = 70/20/10 wt% (two recipes tested)
  - Active material ball-milled with carbon black (no additional carbon black added to slurry formulation)
  - Pristine active material with carbon added just to the slurry
- High molecular weight PVDF (MW *ca*. 1 M) and low molecular PVDF (MW *ca*. 280 K) were each investigated. Levels of NMP in the slurry were investigated for ease of fabrication.
- Half-cells (2325 coin cell) were used to assess electrochemical performance of the cathodes. Gen2 electrolyte (1.2 M $LiPF_6$ in EC/EMC (3/7 wt) was used.
- Electrode loading: approximately 0.6 mAh/cm^2
- Rate test:
  - Cycle at C/20 for 3 formation cycles;
  - Charge C/10; discharge C/10 to 5C
  - C_{rate} based on a capacity of 200 mAh/g.
  - Cut-off voltage: Charge 4.8 V; Discharge 1.0 V